

Testing of an Automatic Temperature Recording System for an Isoperibolic Solution Calorimeter

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Abstract

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An isoperibolic solution calorimeter, essentially identical to an LKB 8721-1 instrument, has been fitted with a simple thermistor circuit which provides for an automatic and precise recording of temperature. Experiments with the "tris"-HCl test reaction have been performed. $\Delta H = -(30.632 \pm 0.008 (\pm 2 \text{ sdm}) \text{ kJ mol}^{-1}$ at 293.15 K, $\Delta H = -(29.768 \pm 0.003) \text{ kJ mol}^{-1}$ at 298.15 K and $\Delta H = -(28.893 \pm 0.007) \text{ kJ mol}^{-1}$ at 303.15 K. $\Delta C_p = (173.9 \pm 1.3) \text{ J K}^{-1} \text{ mol}^{-1}$ at 298.15 K.

Several years ago an isoperibolic solution and reaction calorimeter was developed at this laboratory [1]. The instrument was subsequently improved and later became the basic part of the LKB 8700 calorimeter system [2]. In this paper we describe an automatic temperature recording system used with this type of calorimeter.

The properties of the instrument have been tested with the "tris"-test reaction and the obtained values have been compared with our earlier results [2-5] and the values certified by the National Bureau of Standards [6]. The calorimeter has recently been used in several series of measurements involving aqueous solution processes [7, 8].

Description and function of the instrument

Calorimetric vessel and thermostat

The calorimetric vessel, volume 100 cm³, is made from thin-walled glass. It is fitted with a thermistor (Victory Eng. Corp., ca. 2 000 Ω at 25°C), a 50 Ω manganine heater and a combined stirrer and ampoule holder. The vessel and the surrounding nickel plated brass can are closely similar to corresponding parts of the LKB 8721-1 reaction and solution calorimeter. The manganine heater, ampoule breaking device, stirrer drive, and the water thermostat were all obtained from LKB-Produkter.

Temperature measurement and calibration circuit

Unlike the LKB calorimeter the present instrument does not make use of a balanced Wheatstone bridge for the temperature measurements. Instead the circuit shown schematically in Fig. 1 was used. A constant current generated by A is passed through the thermistor B in the calorimeter, and the resulting potential is largely compensated by a constant potential source (C). The remaining voltage is amplified by a Kiethley 150 B Microvolt Ammeter (D) and the signal is read by a five place digital voltmeter (E) (SE

Laboratories Ltd. SM 213 Mk3) with an input resistance $> 5\,000 \text{ M}\Omega$. During a measurement the voltage signal as read by the voltmeter is printed out each five seconds with a paper tape punch (F ; Mohawk Data Science Corp. 2110R). The units A , C and the set-up for measurement of calibration energy, thermistor current and compensation potential were designed and built at this laboratory by Mr S. Hägg.

It is essential that the thermistor current and the compensation potential are maintained constant. The vital electronic components of A and C are therefore thermostatted at about 60°C, with a maximum temperature variation of 0.01 K.

Thermistor current (ca. 200 μA) and compensation voltage (0.1-1 V) can be measured by replacing the thermistor with a built-in precision resistor (G ; 2 000 Ω , General Resistance Econistors 8E16). The potential over G can be measured both with and without compensation as shown in Fig. 1. This allows determination of the current to a resolution of 10^{-8} A and the compensation voltage to 10^{-5} V .

With the arrangement shown in Fig. 1 the temperature is read by the voltmeter with a resolution of $7 \times 10^{-5} \text{ K}$. Analysis of drift data, like those recorded during a fore or after period of a calorimetric experiment, indicates a resolution of measured temperature changes equal to $2 \times 10^{-5} \text{ K}$. The temperature change observed when an empty dry ampoule is broken in water was found to be $(-3 \pm 1) 10^{-5} \text{ K}$ (5 experiments; $\pm 2 \text{ sdm}$). The practical sensitivity of the instrument is thus considered to be $2 \times 10^{-5} \text{ K}$.

Current for the calibration heater (H) in the calorimeter vessel is supplied by the constant current source (I) of an LKB micro-calorimeter control unit (LKB instrument group 10700). This unit also contains a timer for regulating the length of the heating period.

Calculation procedures. Corrections

All calculations were performed with a Hewlett Packard 9810A desk-top calculator equipped with a tape reader. The voltage values obtained from the thermistor circuit are recalculated to corresponding temperature values by use of eq. (1) and the values for thermistor current and compensation potential.

$$R = A \cdot e^{B/T + C/T^2} \quad (1)$$

A , B and C are constants which were determined in separate calibration experiments, where the calorimeter vessel was equilibrated while immersed in a thermostatted water bath without stirring. For these experiments, which were performed at several temperatures in the range 293-303 K, a calibrated Pt resistance thermometer was used as standard. The absolute temperature values calculated by eq. (1) are believed to be accurate within 0.01 K.

The thermistor values recorded on the punched tape are automa-

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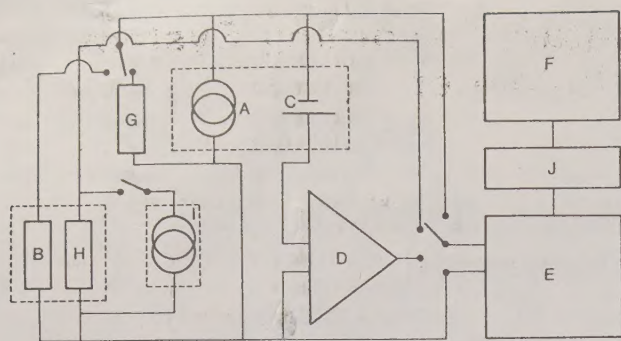


Fig. 1. Schematic drawing of temperature measurement and data acquisition system. A, constant thermistor current supply; B, thermistor; C, compensation potential source; D, amplifier; E, digital voltmeter; F, tape punch; G, dummy resistance; H, calibration heater; I, calibration current source; J, interface unit.

tically read into the memory of the calculator which is programmed for eq. (1) and the equations used in the calculation of the heat exchange term. Corrected temperature changes in an experiment were calculated both by the Regnault-Pfaundler integration method and by the Dickinson extrapolation method.

Calibration energies were calculated from a predetermined resistance value for the heater, the voltage over the heater as measured by the voltmeter and by the heating time present for the calibration current source. The accuracy by which the heater resistance is measured is judged to be $\pm 0.01\%$. Leads between the heater and the contacts on the calorimeter lid have a resistance which is 0.03% of that of the manganine coil. In the calculations it is assumed that 50% of the energy evolved in the leads is conducted to the calorimeter.

The resistance of the calibration heater will increase slightly during a calibration experiment following the temperature increase of the manganine coil. Depending on the heating current steady state resistance values are reached after 15–25 sec (10–125 mA). With the heating current used in the tris-test experiments, 125 mA, the difference in resistance between the cold heater and the steady state values was 0.06%. In the test experiments the heating time was ca. 180 sec leading to an effective resistance value which is 0.003 per cent lower than the steady state value.

The timer of the calibration unit was calibrated using a Seltran Digital Counter SF (± 100 ppm) and small corrections (< 0.01 sec) were applied to the nominal heating time.

Test experiments

Materials

Dilute hydrochloric acid, 0.100 mol dm⁻³, was prepared from glass distilled water and Merck standardized hydrochloric acid (Titrisol). Two batches of "tris" (tris(hydroxymethyl)aminomethane) were used; "sample G" and a sample obtained from National Bureau of Standards, Washington D.C. (SRM 724). Sample G was purified at this laboratory as described earlier [3].

The molecular weight used for tris was 121.137 and sample weights were corrected to masses by using the density 1.35 g cm⁻³ [9].

Calorimetric measurements

The solution experiments with tris in dilute HCl were performed as described earlier [5], i.e. essentially in accordance with the

recommendations of the U.S. Calorimetry Conference [9]. The amount of tris dissolved in the calorimetric liquid, volume 100 cm³, was (0.5 ± 0.1) g.

Results

Table I summarizes results from two series of electrical calibration experiments. Each series was performed as repeated heating and cooling steps without any change of the calorimetric liquid. For each series the individual experiments were nearly identical with respect to starting temperature, electrical heat effect and heating time.

In the first series (nine experiments) the calorimeter was charged with 100 cm³ of HCl solution (0.1 mol dm⁻³) whereas in the second series (10 experiments) pure water was used as calorimetric liquid. Different stirrers were used in the two series and the derived calibration constants are therefore not comparable. P , Q and ΔT are approximate values for the electrical heat effect, the electrical energy and the temperature change, respectively.

$\bar{\epsilon}_{RP}$ and $\bar{\epsilon}_D$ are the mean values for the calibration constants where the heat exchange correction terms are calculated by the methods of Regnault-Pfaundler and Dickinson, respectively.

It is seen that by using the Regnault-Pfaundler method ϵ values were determined with a precision of 0.002% (± 2 sdm) when the temperature change was 0.29 K. The corresponding precision was 0.04 per cent when the temperature change was 0.10 K.

For the first series of experiments we note that there is a small but significant difference between $\bar{\epsilon}_{RP}$ and $\bar{\epsilon}_D$, 0.02%. For the second series a similar, but insignificant difference is found.

Results of the tris test experiments are shown in Table II. Measurements were performed at three different temperatures, 293.15, 298.15 and 303.15 K. For sample G two series of measurements were made at each temperature. They were performed at a time interval of about one year using two different calorimetric vessels. The NBS sample was measured at 298.15 K.

Electrical calibrations were performed after each solution experiment and covered the same temperature range ± 0.01 K. The enthalpy values calculated for the isothermal process will thus refer to the starting temperature of the solution experiment. Small temperature corrections were applied to correct the values to the nominal temperatures. Small corrections were also applied for effects in connection with the initiation of the solution process. In separate experiments the enthalpy change for the breaking of the sample ampoule was determined to be $-(0.007 \pm 0.004)$ J. Enthalpy changes for evaporation of water with ampoule breaking were estimated in each experiment. Corrections were in the range 0.015–0.025 J.

For all experiments (solution and calibration experiments) heat exchange correction terms were calculated both by the Regnault-Pfaundler method and by the Dickinson method. A small but significant difference between the ΔT values evaluated by the two methods was found both for calibration and for solution experiments; cf. results of the separate series of calibration experiments, Table I. However, when ΔH values were calculated, using the two sets of ΔT values, differences were insignificant and

Table I. Electrical calibration experiments

Series	P/W	Q/J	$\Delta T/K$	$\bar{\epsilon}_{RP}/J K^{-1}$	$\bar{\epsilon}_D/J K^{-1}$
1	0.6	127	0.29	441.94 ± 0.01	442.02 ± 0.02
2	0.4	46	0.10	444.38 ± 0.19	444.47 ± 0.15

Table II. Enthalpies of solution of tris in 0.100 mol dm⁻³ HCl

Temp./K	-Δ <i>H</i> _{soln} /kJ mol ⁻¹ (± 2 sdm)		
	Sample G	Sample G	NBS sample
293.15	30.6317	30.6109	
	30.6414	30.6394	
	30.6520	30.6228	
	30.6227	30.6257	
	30.6241	30.6406	
	30.6800		
	30.6310	Mean 30.628 ± 0.011	
	30.6590		
	30.6521		
	Mean 30.646 ± 0.013		
298.15	29.7702	(29.7363) ^a	29.7649
	29.7667	29.7713	29.7707
	29.7655	29.7647	29.7607
	(29.7191) ^a	29.7596	29.7727
	29.7751	29.7668	29.7629
	29.7773		29.7672
	29.7663	Mean 29.766 ± 0.005	
	Mean 29.770 ± 0.004		Mean 29.767 ± 0.004
303.15	28.8927	28.8976	
	28.9130	28.8719	
	28.9244	28.8810	
	28.9240	28.9047	
	28.9186	28.8756	
	28.9310	28.8900	
	28.9240		
	28.9267	Mean 28.887 ± 0.011	
	28.9169		
	Mean 28.896 ± 0.008		

^a Not included in the mean value of the series.

random. Δ*H* values listed in Table II are averages between the two methods.

Inspection of Table II shows that at each temperature there is no significant difference between the mean values for the different series. Weighted mean values are Δ*H* = -(30.632 ± 0.008) (± 2 sdm) kJ mol⁻¹ at 293.15 K, Δ*H* = -(29.768 ± 0.003) kJ mol⁻¹ at 298.15 K and Δ*H* = -(28.893 ± 0.007) kJ mol⁻¹ at 303.15 K. From these values, using a linear least squares treatment, the Δ*C_p* value for the tris test reaction was calculated to be Δ*C_p* = (173.9 ± 1.3) J K⁻¹ mol⁻¹ at 298.15 K.

In a few experiments CO₂ was bubbled through the HCl solution for 2 h before it was charged into the calorimeter and used with the tris reaction. Interchangeably with these experiments, performed at 298.15 K, measurements were made under standard conditions.

For the experiments conducted under standard conditions a normal value was obtained, Δ*H* = -(29.769 ± 0.007) kJ mol⁻¹ (3 experiments), whereas a slightly lower value was found when CO₂ was present, Δ*H* = -(29.723 ± 0.024) kJ mol⁻¹ (3 experiments).

Discussion

Precision

From the results it is evident that the present method is at least as precise as the corresponding method using a manually operated thermistor bridge, cf. e.g. ref. [5]. Similar to the latter study we note here the highest precision for measurements performed close to the ambient temperature, ca. 297 K.

Accuracy

It is estimated that the possible error in the assigned value for the heater resistance is 0.02%. The error in the heat exchange correc-

tion term is believed to contribute ≤ 0.02% to the enthalpy value. The sum of other possible systematic errors (bulb breaking, vapour space correction, weighing errors, determination of absolute temperature) is judged to be ≤ 0.03%. With these assumptions we estimate the probable systematic error in the Δ*H* values for the tris reaction to be ± 0.012 kJ mol⁻¹ in the temperature ranged investigated.

From the results shown in Table II it is evident that there is no significant difference between the two samples of tris. This confirms our earlier experience [3, 5] that the purification procedure used for tris will lead to a thermodynamically well defined material.

Comparison with earlier results

The present value for 298.15 K, Δ*H* = -(29.768 ± 0.003) kJ mol⁻¹, is slightly higher than results of most series of measurements obtained previously using the standard LKB instrument or its prototype; e.g. -(29.752 ± 0.008) [2], -(29.757 ± 0.016) [4], -(29.744 ± 0.008) [5] kJ mol⁻¹, respectively (uncertainties are ± 2 sdm). However, considering the possible systematic and random errors there appears to be no significant difference between the value reported here and the earlier results. As pointed out previously [2] the value for the tris reaction originally reported from this laboratory [3], Δ*H* = -29.73 kJ mol⁻¹, is considered low, partly due to a calculation error.

The present value is in full agreement with the "NBS certified value" [6], Δ*H* = -(29.771 ± 0.031) kJ mol⁻¹ (± overall uncertainty).

The present Δ*C_p* value (173.9 ± 1.3 J K⁻¹ mol⁻¹ at 298.15 K) is very close to our earlier value [4] (174.1 J K⁻¹ mol⁻¹) and to the NBS value (173.8 ± 2.8) J K⁻¹ mol⁻¹.

The NBS values were arrived at after extensive studies by Prosen and Kilday using a Pt lined adiabatic calorimeter [6]. The precision (± 2 sdm) of their Δ*H* value at 298.15 K is ± 0.005 kJ mol⁻¹. Unlike the case with our instrument, the uncertainty in their value for the calibration energy is almost negligible and no heat exchange correction is needed with the adiabatic method employed. The comparatively large uncertainty the NBS workers assigned to their value, ± 0.031 kJ mol⁻¹, was chosen mainly because of rather strange thermal effects which they observed in some of their experiments. If their calorimeter was closed considerably higher values were found (-Δ*H* ≥ 30.5 kJ mol⁻¹) and if the solution process was performed in the presence of O₂ and CO₂ much more exothermic values were obtained.

At our laboratory no such phenomena have been observed. Olofsson et al. [10] carried out the tris reaction at 298.15 K in a closed bomb calorimeter (stainless steel vessel, isoperibolic calorimeter). Their value was normal, Δ*H* = -(29.79 ± 0.08) kJ mol⁻¹ (± 2 sdm).

The Δ*H* value found for the tris reaction when conducted with CO₂ saturated HCl solution was slightly less exothermic than the normal value. This effect, which also has been noted by Olofsson [11] using a standard LKB 8721-1 calorimeter, may well be due to evaporation of CO₂ during the temperature increase.

From the collected experience at this laboratory, and on chemical grounds, we find no reason to suspect the presence of any side reaction in the tris-HCl solution process when performed in glass or high quality stainless steel vessels. Prosen and Kilday [6] pointed out that there is a large spread among data reported for this reaction. In our opinion this indicates the presence of systematic instrumental or operational errors in several of the values reported.

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